Indian J. Phys. **79** (3), 313-315 (2005)

Note
AN INTERNATIONAL JOURNAL
IJP

$Eu^{3+} \rightarrow Sm^{3+}$ energy transfer in CaS phosphor

Vijay Singh*, Manoj Tiwari[1] and S J Dhoble[2]

*Department of Post Graduate Studies & Research in Physics, Bhoj College, Kotra, Bhopal-462 003, Madhya Pradesh, India

[1]Department of Physics, Bansal Institute of Science & Technology, Bhopal-462 021, Madhya Pradesh, India

[2]Department of Physics, Kamla Nehru College, Nagpur-440 009, Maharastra, India

E-mail : vijayjiin@hotmail.com

Received 26 May 2004, accepted 2 January 2005

Abstract : CaS phosphors activated with Eu^{3+} and Sm^{3+} ions, were prepared by using solid-state diffusion method. Emission and excitation spectra were recorded at room temperature on CaS:Eu and CaS:Eu,Sm phosphors with the aim of their photoluminescence characterization as well as the energy transfer process. CaS phosphor shows the strong emission of Sm^{3+} ions in red region of spectrum due to energy transfer from Eu^{3+} to Sm^{3+} ions. Thermoluminescence study was also carried out of CaS:Eu and CaS Eu,Sm phosphors.

Keywords : Photoluminescence, doping, CaS:Eu,Sm phosphor

PACS Nos. : 78.55 Hx, 61.72.Ww

Alkaline earth sulphide has been known as excellent phosphor for a long time [1]. Rare earth and non-rare earth-doped sulphide phosphors have been investigated by many research workers [2,3]. These phosphors have great potential as broad band light source in both powder and thin film luminescent devices [4]. Recently, it has attracted more attention because of the potential uses in many fields, for example, cathode ray tubes, infrared sensors, thermoluminescence, electroluminescence panels [5]. Calcium sulphide doped with double rare earth ions is a kind of infrared stimulable phosphor. The dopants may act as trapping/recombination/luminescence centers in the host, and also play an important role in energy storage [6]. The incorporation of two or more activators in a host is to see how far they modify the luminescence characteristics. The trivalent europium and samarium are widely used as an activator in a large variety of luminescent inorganic materials. Recently, much work has been devoted to trivalent rare earth-doped phosphors in different hosts due to their potential device applications in opto-electronics [7]. Photo-stimulable rare earth doubly-doped alkaline earth sulphide phosphors such as SrS:Eu,Sm [8], CaS:Ce,Sm [9] and MgS:Ce,Sm [10], were conventionally used as infra-red sensors [11] and expected to be developed as an erasable and rewritable optical memory medium [12]. Energy transfer processes are very important in solid-state luminescence system because they provide an enhancement of the luminescence emission.

In this note, the photoluminescence and thermoluminescence spectra of CaS:Eu and CaS:Eu,Sm have been studied. The energy transfer processes have been investigated by the emission spectra.

Calcium sulphide phosphor was obtained using solid-state reaction between activator (europium and samarium) and calcium sulphate using Na_2SO_4 as flux and fired at 1000^0C in a muffle furnace for 2 hours. The reducing agent was AR grade carbon powder used in synthesis. After heat treatment, the resultant powder pulverized in a dry atmosphere and stored, keeping in view the extreme purity as the main consideration in preparation. X-ray diffraction photograph technique was used for checking proper crystallization of powder. The details of phosphor preparation are the same as reported in earlier papers [13-15]. Photoluminescence spectra were recorded on FP-750 spectrofluorometer (Jasco, Japan) with red sensitive PM tube. Thermoluminescence glow curves were also recorded with the usual setup consisting of a small metal plate heated directly using a temperature programmer, photomultiplier (931B), dc amplifier and a millivolt recorder.

Corresponding Author

PL in CaS:Eu,Sm phosphor :

Sm^{3+} emission in CaS shown in Figure 1 (curve b), prominent PL emission peaks are observed at 493, 573, 613, 650 nm, when excitation wavelength is 270 nm (excitation spectra shown in Figure 1 curve a). These PL peaks are observed due to the transition of $^4G_{5/2} \rightarrow {}^6H_{3/2}$, $^4G_{5/2} \rightarrow {}^6H_{5/2}$, $^4G_{5/2} \rightarrow {}^6H_{7/2}$ and $^4G_{5/2} \rightarrow 6H_{9/2}$ of Sm^{3+} ion in CaS lattice. Furthermore, they have associated with the line structure in the excitation spectrum to the transitions within the $4f^5$ configuration and the broad bands to the $4f^5 \rightarrow 4f^45d$ transition of Sm^{3+} in sulphides. Recently, Jaaniso and Bill [16] reported room temperature persistent spectral hole burning (PSHB) for the Sm^{2+}-doped BaFCl crystal for the first time. Since then, room temperature PSHB for Sm^{2+} doped into several different host materials has been reported [17-19]. The optical properties of the Sm^{2+} ion have also been widely studied [20,21] as it is one of the most important candidates for producing high temperature PSHB materials. PSHB mechanisms are closely related to the optical properties of ions doped into the crystals or glasses. Therefore, establishment and enhancement of Sm^{3+} emission in phosphors is an important field for the development of red emission of Sm^{3+} as opto-electronics materials for different applications. The emission spectra of CaS:Eu^{3+},Sm^{3+} Figure 1. (curve c) show the prominent peaks, observed at 573 and 613 nm (excitation wavelength 270 nm). The 493 nm peak intensity decrease due to the Eu co-doped with Sm^{3+}, while 573 and 613 nm peaks of Sm^{3+} ion intensity increase by two fold due to energy transfer from Eu^{3+} to Sm^{3+} ions.

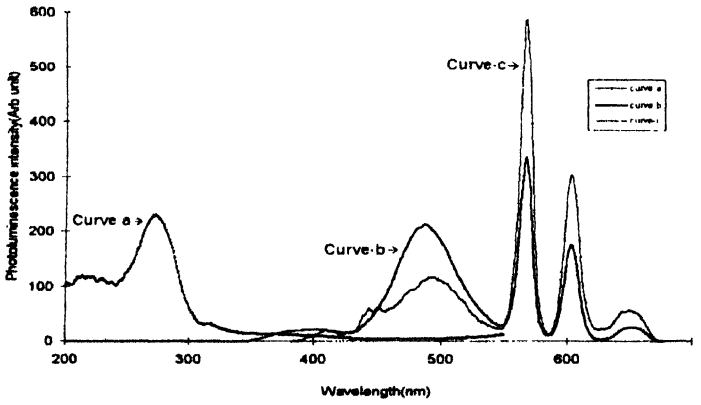

Figure 1. Photoluminescence spectra of CaS:Sm(0.1 mole%) and CaS:Eu(0.1 mole%),Sm(0.1 mole%).
Curve-a : Excitation spectra of CaS:Sm(λ_{em} = 573 nm);
Curve-b : Emission spectra of CaS:Sm(λ_{ex} = 270 nm);
Curve-c : Emission spectra of CaS:Eu,Sm (λ_{ex} = 270 nm).

TL in CaS:Eu,Sm phosphor :

Figure 2 shows the TL glow curve of CaS host doped with Eu and Sm. Curve-a represents the TL glow curve of CaS:Eu phosphor. A weak TL peak is at 448K and a strong TL peak at 598K are observed. Curve-b shows the TL glow curve of CaS:Eu,Sm phosphors. Two prominent peaks are observed at 373K and 598K, its intensity is around 1.5 times greater than those of CaS:Eu phosphor. Curve-c shows the TL glow curve of CaS:Sm exposed to γ-Rays (225 Gy). In CaS:Sm phosphor, TL glow curve, shows a prominent TL peak at 448K and a weak TL peak around 598K. The 448K TL peak shows only one type of defect center and is very strongly formed in the phosphor. Some of the defect centers are released at 598K. The concentration of these types of centers is very less.

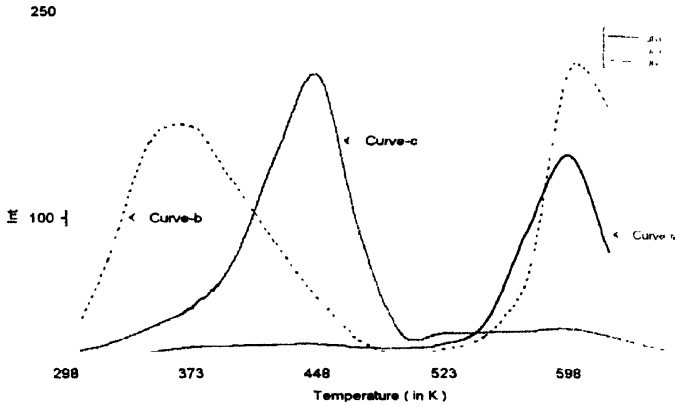

Figure 2. TL glow curve of various phosphors exposed to gamma-rays (225 Gy)
Curve-a : CaS:Eu(0.1 mole%) , Curve-b : CaS:Eu(0.1 mole%) Sm(0.1 mole%); Curve-c : CaS:Sm(0.1 mole%)

By co-doping CaS:Sm with Eu and exciting it to same wavelength (270 nm) the emission peaks are observed at same wavelength as those of CaS:Sm. However, increase in peak intensity is observed which may be due to energy transfer from Eu^{3+} ion to Sm^{3+} ions. This mechanism of energy transfer supports effectively one of the syntheses of solid-state diffusion of CaS phosphor. Hence, CaS:Eu,Sm phosphor may be useful as red emission phosphor in opto-electronic devices.

TL glow curve of CaS:Eu,Sm phosphor shows two prominent peaks at 373K and 598K. The 598K TL peak of CaS:Eu,Sm phosphor intensity is around 1.5 times higher than 598K TL peak of CaS:Eu phosphor. Hence, in CaS:Eu,Sm phosphor, more defects are formed due to gamma irradiation.

Acknowledgments

The authors are thankful to Dr. B. C. Bhatt, Head, Radiological Physics & Advisory Division, BARC, Trombay, Mumbai for permitting us to use facilities available at the center.

References

[1] A Wecht, M Wacte, M H Higcon *et al* *J. Lumin.* 24 25 917 (1981)

[2] Wenhui Fan and Yougchang Wang *J. Applied Phys. Lett.* 85 451 (1999)

] Han Choi, Chang-Hong and Chang-Hong Pyun *J Solid State Chem.* **138** 149 (1998)

] I V F Viney, B W Arenton, B Ray and J W J Brighwell *J Crystal Growth* **117** 806 (1992)

] Mai Pham-Thi *J. Alloys Compounds* **225** 547 (1995)

] Z Hua, L Salamanca-Riba, M Wuttig and P K Soltani *J Opt. Soc Am* **B10** 1464 (1993)

] P Dorenbos *J. Lumin.* **91** 91 (2000)

[8] L H Robins and J A Tuchman *Phys. Rev* **B57** 12094 (1998)

[9] K Chakraborti, V K Mathur, L A Thomas and R J Abbundi *J Appl Phys.* **64** 2021 (1989)

] K Chakraborti, V K Mathur, J F Rhodes and R J Abbundi *J. Appl Phys* **64** 1363 (1988)

] S P Keller, J E Mapes and G Cheroff *Phys. Rev.* **108** 663 (1957)

[12] S Jutamulia, G M Storti, J Lindmayer and W Seiderman *Appl Opt.* **30** 2879 (1991)

[13] R N Dubey, O N Awasthi, V Singh and M Tiwari *Indian J. Pure Appl. Phys.* **40** 54 (2002)

[14] R N Dubey, M S Qureshi, V Singh and M Tiwari and S J Dhoble *Indian J. Pure Appl Phys* **41** 40 (2003)

[15] M Tiwari, V Singh, S J Dhoble and O N Awasthi *Indian J. Pure Appl Phys.* **41** 894 (2003)

[16] R Jaaniso and H Bill *Euro Phys Lett* **16** 569 (1991)

[17] K Hirao, S Todoroki and N Soga *J. Lumin.* **55** 217 (1993)

[18] L Zhang, S Huang and J Yu *J. Lumin* **45** 301 (1990)

[19] M Nogami and Y Abe *Appl Phys Lett.* **64** 1227 (1994)

[20] M Nogami and Y Abe *Appl Phys.* **80** 409 (1996)

[21] K Jang, I Kim, H Seo, S Park, S Lee, and W S Back *J. Phys. Condens Matter* **13** 3223 (2001)